Chapter 12
Rheology of Glass-Forming Melts

12.1 Introduction

Rheology, as indicated by its very name (*rheos*: to flow) is in its classical sense the science describing flow processes of matter, i.e., the displacement of the building units of a substance as a whole or parts of it under the influence of an applied force. The modern interpretation of rheology includes both the meaning as given above as well as the description of relaxation kinetics, i.e., the response of a system after an initially applied stress (or, more general, an external influence) has ceased to operate. An instructive and technically important example of the latter process is relaxation of strains (strain birefringence) in glass-annealing. In the terminology used in Chap. 3, annealing and relaxation of glasses may be considered as particular examples of stabilization processes, i.e., the evolution of an initially frozen-in system of increased disordered to the state of metastable equilibrium characterized by a lower degree of disorder.

Two approaches have been developed in the rheology of glass-forming melts:

- A *phenomenological approach*, based on considerations following from a number of phenomenological models and their combinations;
- A *microscopic approach* involving more or less well-defined molecular model considerations concerning the mechanism of flow.

In the phenomenological approach, the flow and relaxation of condensed matter is described with model dependencies derived from the behavior of different idealized systems. The two basic models, which are used in different combinations, are Hooke's absolutely rigid elastic body and Newton's viscous liquid.

The classical phenomenological models of flow and relaxation of viscoelastic bodies, due to Maxwell, Kelvin, Voigt, Zener and others, can also be obtained as combinations of elementary mechanical elements reflecting the properties of Hookean bodies (elastic spring) and Newtonian fluids (dashpot). An overview on the classical phenomenological model approaches and of their significance in the development in the theory of flow and relaxation for different systems can be

found in the respective literature (see, e.g., Reiner (1956) [659]; Freudenthal (1956) [235]; Wilkinson (1960) [922]; Sobotka (1984) [785] for a general description of rheological models; Treloar (1949) [853]; Stanworth (1953) [793]; Morey (1954) [574]; Alfrey (1955) [7] for the application to glasses and polymer systems). Of exceptional importance was the finding (due mainly to Meixner (1953, 1954) [555, 556]; see also Zener's model described by Dehlinger (1955) [162]) that the most important of the classical rheological models can be derived based on the thermodynamics of irreversible processes in its linear formulation. Zener's model, giving a very general description of viscoelastic bodies, turned out to be a consequence of one of the basic relationships of the thermodynamics of irreversible processes – the so-called dynamic equation of state (for the derivation of Zener's model from this fundamental equation see Meixner's original paper [555] or Haase (1963) [339]). In this sense the phenomenological rheology has no longer to be considered as a random collection of more or less intuitively formulated models of flow and relaxation but as a consequence of another more general phenomenological theoretical approach – the thermodynamic one.

One of the most fruitful and general directions in the microscopic approach to the description of flow turned out to be the Prandtl-Eyring model of flow under shear stress (see Prandtl (1928) [644]; Glasstone, Laidler, and Eyring (1941) [255] and generalizations of this model by Beaver (1986) [56]; Gutzow, Dobreva, and Schmelzer (1993) [332]). From a more general point of view the Prandtl-Eyring model can be interpreted as an activated complex approach in terms of the absolute rate theory. Other important molecular concepts are connected with free volume and hole theories of liquids, with the "thermodynamic" approach in deriving the temperature dependence of the viscosity (developed by Adam and Gibbs (1965) [5]), energetic level models (bond lattice models; Rao and Angell (1972) [656]) with entangled or free draining coil models of polymer solutions (Bueche (1962) [109]) etc. Molecular models of relaxation of glass-forming melts, formulated in terms of two-, three- or multi-dimensional energetic level models were derived by Volkenstein and Ptizyn (1956) [892] (see also Volkenstein (1959) [891]; Mazurin (1986) [543]; Avramov and Milchev (1984 [25], 1988 [26], 1991 [21])). The latter mentioned authors also succeeded in giving a molecular model of vitrification and relaxation of glasses capable of describing memory effects.

A summary of classical attempts in the molecular theory of rheology may by found in the monographs by Frenkel (1946) [233], Glasstone et al. (1941) [255], Bartenev, Frenkel, Sanditov (1982, 1986, 1990) [47, 48, 683], and Melvin-Hughes (1972) [567]; more recent developments in application to polymer systems ("tube-flow" models) are discussed by Doi (1980) [178]. In Frischat's monograph (1975) [237] a summary of model approaches and experimental data can be found concerning diffusion and self-diffusion in inorganic glass-forming systems. A thorough discussion of the different microscopic approaches to viscous flow and molecular models of diffusion including disordered systems is given by Manning (1968) [529]; this problem is also treated in detail by Milchev and Avramov (1983) [559] (cf. also [121]). It turns out that in terms of different molecular models of flow the viscosity and self-diffusion in glass-forming melts can even be described

quantitatively. However, all efforts to interpret relaxation in simple and polymer glass-forming melts, using either linear combinations of Newtonian and Hookean elements or existing molecular models, failed or allowed one only a qualitative description.

An example in this respect is the failure to describe processes of glass annealing by using Maxwell's equation, i.e., a linear combination of elements reflecting Hookean elastic bodies and Newtonian viscous flow. A summary concerning this problem is given by Morey (1954) [574]. In order to overcome the difficulties connected with the description of relaxation in real systems three different attempts have been developed:

- More than one relaxation time is introduced into the description using a set of linear relaxation equations of Maxwellian type with more or less arbitrarily chosen relaxation times. Hereby up to 6–10 Maxwellian exponents are employed in order to reach a quantitatively correct description of the process. This method, described in detail by Mazurin (1986) [543], has been widely employed by Kovacs (cf. Kovacs et al. (1979) [479] and for earlier investigations Treloar (1949) [853]).
- More complicated non-linear empirical dependencies are used, in particular, relations with a time-dependent relaxation time. A classical example in this respect is Kohlrausch's fractional exponent formula which he first proposed in 1876 [462]. It was introduced into the rheology of silicate glass-forming melts by Rekhson and Mazurin (1974, 1977) [542, 662]. Similar time-dependencies were used by Jenckel (1955) [407] in order to model relaxation in organic glass-forming melts and by Williams and Watts for a description of dielectric relaxation (see Mazurin (1986) [543]). Another classical non-linear dependence of this type is the Adams-Williamson annealing equation, employed for many years in the technology of glass annealing [6], (see also Morey (1954) [574]). In a more formalistic but more general way such generalizations can be introduced by the method employed for the description of stabilization in Sect. 3.9 by introducing an effective relaxation time depending on the prehistory of the system.
- A third method in the description of relaxation kinetics consists in the introduction of real Non-Newtonian flow dependencies into the corresponding kinetic equations. In this way, the specific rheological behavior of the relaxing system is directly accounted for. This method was indicated for the first time by Eyring et al. (1948) [839], it was extended by using existing or appropriately modified models of flow by Gutzow et al. (1993) [332]. It can be shown that, in this way, existing empirical dependencies used in the description of the kinetics of relaxation (including Kohlrausch's formula and similar relations capable of describing quantitatively relaxation in real glass-forming systems) can be obtained, which are determined by the particular flow mechanism of the system under investigation.

In analyzing the rheological properties of viscoelastic bodies, the elastic component can be considered as the direct response of the system to external disturbances, while the viscosity reflects its dissipative reaction. Viscoelastic bodies thus represent, with

respect to their rheological behavior, a bridge between matter in different states of aggregation, indicating their similarities despite their qualitative differences (or in the words of Hegel (1817) [351] "water, like air, is fluid but its fluidity is elastic").

The elastic component in the rheological behavior of liquids and glass-forming melts is of importance not only for flow and relaxation but also in processes of crystallization and segregation taking place in them. Consequently, in the description of the kinetics of such processes modifications have to be introduced as compared with phase formation in Newtonian liquids (cf. Chap. 6) or crystallization of Hookean elastic solids (cf., e.g., Sect. 7.7.1). One example, where elastic strains in segregation processes in viscoelastic melts modify the kinetics qualitatively, was given in Fig. 9.3 in Sect. 9.4 (segregation in photo-chromic glasses). In this way, it turned out that a quantitatively correct description of crystallization and phase formation in glass-forming melts, especially in the vicinity of T_g, has to be developed in terms of a theory of phase transformations in viscoelastic bodies.

12.2   Phenomenological Rheology of Glass-Forming Melts in its Linear Approximation

The basic rheological characteristics of a liquid or plastic solid body are given by the dependence of rate of shear flow, $d\gamma/dt$, on shear stress, Π. For Newtonian or ideal liquids the relation

$$\frac{d\gamma}{dt} = \frac{\Pi}{\eta} \tag{12.1}$$

holds, where η is the Newtonian shear viscosity of the melt. It depends on temperature but not on the applied stress. In the practice of rheological investigations it turns out, however that Eq. (12.1) is usually fulfilled only in the limiting case of very small applied stresses ($\Pi \rightarrow 0$). Real liquids deviate from Newtonian liquids in two ways: $d\gamma/dt$ increases either faster or slower than the linear dependence as described by the above equation allowing one to develop a classification of Non-Newtonian liquids into two classes discussed in the following section.

The second classical idealization used in rheology is the model of a Hookean absolutely elastic body. The relation between stress and deformation can be written for this case in the form

$$\gamma = \frac{1}{G^*}\Pi \ , \tag{12.2}$$

where G^* is the modulus of elasticity for the particular type of deformation. In a solid body without viscous flow, the relation $\Pi = G^*\gamma$ is fulfilled at any time, moreover, the relation

$$\frac{d\gamma}{dt} = \frac{1}{G^*}\frac{d\Pi}{dt} \tag{12.3}$$

holds. In the presence of viscous flow strains will disappear with time at a rate depending on the actual value of Π.
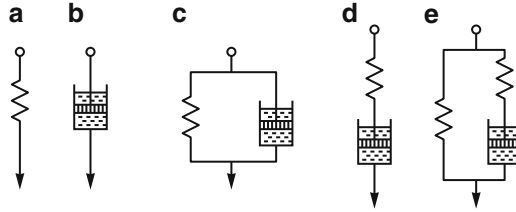
Fig. 12.1 Mechanical models, combinations of springs and dashpots, reflecting the properties of viscoelastic bodies according to several classical models. It is assumed that the reaction of the spring (**a**) is described by Hooke's law, while the dashpot (**b**) has the properties of a Newtonian viscous liquid. The different combinations refer to (**c**) Kelvin's, (**d**) Maxwell's and (**e**) Zener's bodies

If we make the simplest possible assumption, that the rate of change of the strain is proportional to the strain itself, then we get, by a combination of above equations,

$$\frac{d\Pi}{dt} = G^* \frac{d\gamma}{dt} - \frac{\Pi}{\tau_R} \, , \tag{12.4}$$

where

$$\tau_R = \frac{\eta}{G^*} \tag{12.5}$$

is the already discussed characteristic time scale of the process – Maxwell's time of relaxation (cf. Sect. 2.4.3). Note that above given equations, Eqs. (12.1) and (12.2), are obtained from Eq. (12.4) as special cases (for $d\Pi/dt = 0$, respectively, $d\gamma/dt = 0$). Equation (12.4) may be rewritten in the form

$$\frac{d\gamma}{dt} = \frac{\Pi}{\eta} + \frac{1}{G^*} \frac{d\Pi}{dt} \, , \tag{12.6}$$

which is the equation of the so-called Maxwell body.

Another well-known classical relation, the Kelvin-Voigt equation, follows if, in the second term on the right hand side of Eq. (12.6), Π is replaced by $\Pi = G^* \gamma$ and afterwards $d\gamma/dt$, again, by a linear dependence of the form $d\gamma/dt = -\gamma/\tau_R$. One gets

$$\frac{d\gamma}{dt} = \frac{\Pi}{\eta} - \frac{1}{\tau_R} \gamma \, . \tag{12.7}$$

It follows that Maxwell's and Kelvin-Voigt's equations are linear combinations of Eqs. (12.1) and (12.3). A mechanical interpretation of these and of a further rheological dependence (Zener's equation) in terms of combinations of the basic models is given in Fig. 12.1.

The classical rheological models – Hooke's, Newton's, Maxwell's and Kelvin-Voigt's bodies – can be considered as particular cases of a more general rheological equation – Zener's equation. This equation can be derived, as mentioned in the preceding section, by the methods of the linear thermodynamics of irreversible

processes. It is equivalent to the dynamic equation of state. Zener's equation may be
written in the form (see Meixner (1953) [555]; Haase (1963) [339])

$$\frac{d\gamma}{dt} = \frac{G^*}{\kappa\eta}\Pi + \frac{\eta}{\zeta^*G^*}\frac{d\Pi}{dt} - \frac{1}{\tau_R}\gamma \, , \qquad (12.8)$$

where κ is the modulus of bulk elasticity (compressibility) and ζ^* Stokes's bulk
viscosity (cf. Haase (1963) [339]).

According to existing theoretical estimates (see Tobolsky (1960) [838]; Landau
and Lifshitz (1953 [492], 1957 [495])) the relations

$$\frac{\zeta^*}{\eta} = \alpha_1 \cong 3 \, , \qquad (12.9)$$

$$\frac{\kappa}{G^*} = \alpha_2 \cong 2 \qquad (12.10)$$

hold and we obtain in a good approximation

$$\frac{d\gamma}{dt} = \frac{1}{2\eta}\Pi + \frac{1}{3G^*}\frac{d\Pi}{dt} - \frac{1}{\tau_R}\gamma \, . \qquad (12.11)$$

It is evident that

- At small γ-values, i.e., at

$$\Pi/2\eta \gg (1/3G^*)d\Pi/dt - \gamma/\tau_R \, ,$$

  Newton's equation, Eq. (12.1), follows;
- At high γ-values , i.e., at

$$\Pi/2\eta - \gamma/\tau_R \gg (1/3G^*)d\Pi/dt \, ,$$

  the Kelvin-Voigt equation, Eq. (12.7), is obtained;
- At high $(d\Pi/dt)$- and small γ-values both Hooke's equation, Eq. (12.3), for

$$(1/3G^*)d\Pi/dt \gg \Pi/2\eta - \gamma/\tau_R \, ,$$

  and Maxwell's relation, Eq. (12.6), for

$$\Pi/2\eta + (1/3G^*)d\Pi/dt \gg \gamma/\tau_R$$

  are found.

In the subsequent analysis of special cases we omit the numerical factors 2 and 3
for simplicity of the notations.

The above equations may be also applied to the description of flow in sys-
tems consisting of two or more building units. Following Arrhenius and Eyring

(see Hirschfelder et al. (1954) [366]) the viscosity of a two-component system with the molar fractions of the two components x, respectively, $(1 - x)$ may be written in the form

$$\ln \eta = x \ln \eta_1 + (1 - x) \ln \eta_2 , \tag{12.12}$$

where η_1 and η_2 are the viscosities of the pure components for the same thermodynamic conditions. Since the modulus of elasticity, G^*, changes only slightly from one substance to another, a similar expression for the relaxation time, τ_R, may be obtained in the form

$$\ln \tau_R = x \ln \tau_{R1} + (1 - x) \ln \tau_{R2} . \tag{12.13}$$

12.3 Analysis of Special Cases

The solutions of Eqs. (12.1), (12.3), (12.6) and (12.7) give the degree of deformation as a function of time for the different models considered. With the boundary and initial conditions ($\Pi = \Pi_0 =$ const.) and ($\gamma(t = 0) = 0$) we have, for example,

$$\gamma(t) = \frac{\Pi_0}{\eta} t \tag{12.14}$$

for Newton's liquid and

$$\gamma(t) = \frac{\Pi_0}{G^*} \left[1 - \exp \left(-\frac{t}{\tau_R} \right) \right] \tag{12.15}$$

for Kelvin-Voigt's model. A derivation of Eq. (12.15) with respect to time yields

$$\frac{d\gamma(t)}{dt} = \frac{\Pi_0}{G^* \tau_R} \exp \left(-\frac{t}{\tau_R} \right) . \tag{12.16}$$

It follows that the rate of deformation in a viscoelastic body, described by Kelvin-Voigt's equation, is smaller by a factor $\exp(-t/\tau_R)$ than for the same process taking place in a Newtonian liquid.
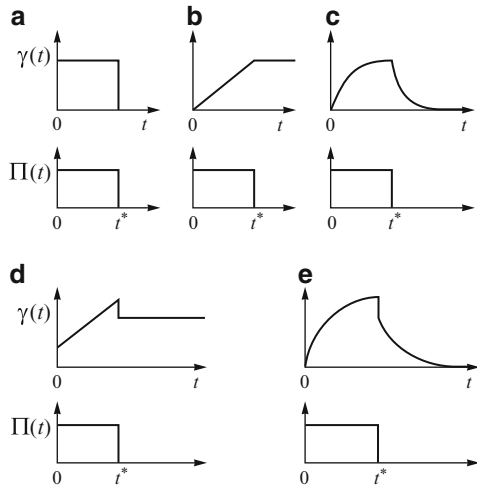
Another important special case is the relaxation of a system after an applied external strain becomes suddenly equal to zero. In this case, Zener's as well as Kelvin-Voigt's equations, are reduced to

$$\frac{d\gamma(t)}{dt} = -\frac{1}{\tau_R} \gamma(t) \tag{12.17}$$

with the solution (for $\gamma(t = 0) = \gamma_0$)

$$\gamma(t) = \gamma_0 \exp \left(-\frac{t}{\tau_R} \right) . \tag{12.18}$$

In application to the description of the reaction of a system, when an external strain
is suddenly applied, the characteristic time, τ_R, is usually denoted as retardation
time and the respective process as a process of retardation. For the considered simple
models relaxation and retardation times coincide.

Another type of reaction of a system, which is of interest in applications,
consists of the kinetics of relaxation of stress at constant deformation (i.e., at
$\gamma = \gamma_0 = $ const.). From Eqs. (12.1) and (12.7) it becomes obvious that Newton's
and Kelvin-Voigt's equations lead to quite unrealistic time-dependencies of $\Pi(t)$
for this case ($\Pi = 0$, $\Pi = \gamma_0/G^* = $ const.). In contrast, Zener's and Maxwell's
models provide the possibility of stress relaxation, the first one in the form

$$\frac{1}{G^*}\frac{d\Pi}{dt} = -\frac{1}{\tau_r}\left(\frac{\Pi}{G^*} - \gamma_0\right)$$

(12.19)

with the solution

$$\Pi(t) = G^*\left[\gamma_0 + \left(\frac{\Pi(0)}{G^*} - \gamma_0\right)\exp\left(-\frac{t}{\tau_R}\right)\right].$$

(12.20)

The problem of relaxation, as described by Maxwell's model, is analyzed in more
detail in Sect. 12.5. The deformation behavior of a system described by different
rheological equations at constant values of Π is illustrated in Fig. 12.2.

Summarizing we may conclude that in the derivation of the classical rheological
models

- Flow is described as in an ideal Newtonian liquid;
- Elastic and flow reactions are connected by linear additive combinations;
- Elastic deformation is assumed to be proportional to the stress (i.e., validity of
  Hooke's law is assumed).

Only a comparison with experimental flow and relaxation curves can show how far the above assumptions are realistic approximations.

In application to glass-forming systems, such comparisons lead to the conclusion that the first assumption is practically never fulfilled for the highly viscous glass-forming melts. Flow of real glass-forming liquids turns out to be, in general, Non-Newtonian; particularly strong Non-Newtonian behavior is found in polymer melts. This result also implies that the kinetics of relaxation of stresses in glasses does not follow the simple Maxwellian kinetics. As far as only relatively small stresses are required to initiate a flow of liquids, Hooke's behavior (assumption 3) is valid in most cases. Thus, in particular, assumptions 1 and 2 require a reconsideration in discussing the rheological properties of glass-forming melts.

12.4   Non-Newtonian Flow Models

In order to retain the classical form of Eq. (12.1) even for Non-Newtonian liquids an apparent (or effective) value of the shear viscosity, $\eta_{(app)}$, is usually introduced, so that the relation

$$\frac{d\gamma}{dt} = \frac{\Pi}{\eta_{(app)}} \tag{12.21}$$

holds. When $\eta_{(app)}$ is a decreasing function of Π the liquid is called pseudo-plastic (or, in polymer literature, shear thinning). In the opposite case, when $\eta_{(app)}$ increases with an increasing value of Π, the liquid is denoted as dilatant (or shear thickening in polymer technology). The pseudo-plasticity or dilatancy of liquids is illustrated in Figs. 12.3a, b. In addition, also the $d\gamma/dt$-dependence corresponding to Bingham's plastic body is given in the same figure as a limiting case of pseudo-plasticity (Fig. 12.3c). It has the form

$$\frac{d\gamma}{dt} = \frac{1}{\eta} (\Pi - \Pi_0) \tag{12.22}$$

In experimental rheology the flow behavior of Non-Newtonian liquids is usually described by a number of empirical relations. Of these equations particularly often employed is the de Waele-Ostwald formula (Ostwald (1925, 1929) [618]; Houwink (1957) [381]):

$$\frac{d\gamma}{dt} = A_0 \frac{\Pi^n}{\eta} . \tag{12.23}$$

It describes the flow kinetics of pseudo-plastic liquids.

Another often used equation is Darcy's relation

$$\frac{d\gamma}{dt} = A_0 \frac{\Pi^{(1/2)}}{\eta} \tag{12.24}$$
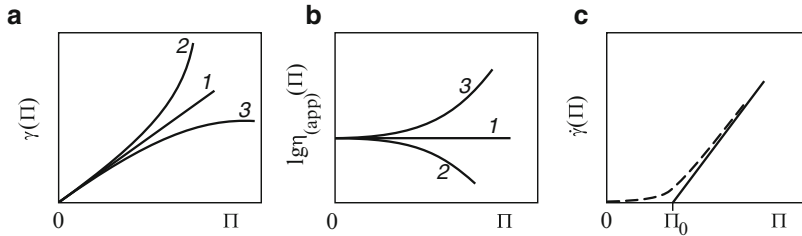
Fig. 12.3 Possible types of flow behavior of liquids (shear-rate vs shear-stress dependencies, schematically). (**a**): Newtonian fluid *(1)*, pseudo-plastic melt *(2)*, dilatant liquid *(3)*. (**b**): Dependence of the apparent shear viscosity on stress: Newtonian liquid *(1)*, pseudo-plastic *(2)* and dilatant *(3)* fluids. (**c**): Shear rate vs shear stress dependence for pseudo-plastic liquids *(dashed curve)* and for Bingham's body approximation *(full curve)*

applied for dilatant liquids. Both equations can be reformulated in terms of Eq. (12.21) with apparent viscosities of the form

$$\eta_{(app)} = \eta \frac{1}{A_0 \Pi^{(n-1)}} \tag{12.25}$$

for the de Waele-Ostwald liquid and

$$\eta_{(app)} = \eta \frac{\Pi^{(1/2)}}{A_0} \tag{12.26}$$

for Darcy's body. It is seen from above dependencies and from Fig. 12.3, that for pseudo-plastic bodies $\eta_{(app)}$ is a decreasing and for dilatant liquids an increasing function of Π.

It can be shown by using well-known expressions for expansion of the sinh-function (Gutzow et al. (1993) [333]) that the de Waele-Ostwald formula, as well as a number of similar dependencies, used for a description of pseudo-plastic bodies, e.g., of the form

$$\eta_{(app)} = \frac{\eta}{(1 + B_0 \Pi^{n-1})} \tag{12.27}$$
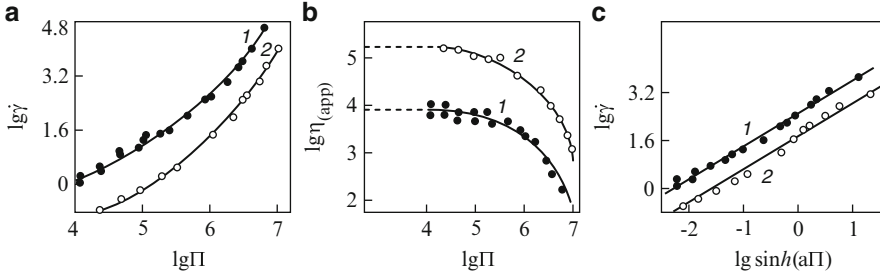
can be obtained as particular cases of a very general formula, known as Prandtl-Eyring's equation

$$\frac{d\gamma}{dt} = \frac{A_0}{\eta} \sinh(a_0^{\odot} \Pi) , \tag{12.28}$$

which yields values of the apparent viscosity of the form

$$\eta_{(app)} = \frac{\eta a_0^{\odot} \Pi}{\sinh(a_0^{\odot} \Pi)} . \tag{12.29}$$

Typical glass-forming melts are, as a rule, pseudo-plastic liquids. In terms of de Waele-Ostwald's formula, widely employed in experimental polymer rheology,

Fig. 12.4 Stress-induced flow of poly(methyl metacrylate) melts as an example of a pseudo-plastic Non-Newtonian liquid. Experimental data are reported by Gul and Kulesnev (1966) [282]: (**a**) $\log(d\gamma/dt)$ vs $\log(\Pi)$ data for two temperatures interpolated by applying the de Waele-Ostwald equation. (**b**) Stress dependence of the apparent viscosity. (**c**) Experimental $(d\gamma/dt)$ vs Π data in coordinates according to the Prandlt-Eyring model; *(black dots)*: data for 523 K; *(circles)* data for 473 K

values of the coefficient n in this equation of the order $n = 1.5$ are usually found. However, the application of the Prandtl-Eyring equation should be preferred: not only does it give a more correct description (cf. Fig. 12.4) but has also the advantage of a molecular foundation, discussed in the next section. It is seen also on Fig. 12.4 that at low Π-values $\eta_{(app)}$ approaches constant values (zero-stress approach to Newtonian liquids). This behavior gives a simple method for determining the Newtonian viscosity of glass-forming liquids by extrapolating the $\eta_{(app)}$-curves to zero stress.

12.5 Linear (Maxwellian) and Non-Maxwellian Kinetics of Relaxation

Maxwell's equation, Eq. (12.6), describes the kinetics of relaxation of stresses, Π, in a body at a constant deformation, γ, in the form

$$\frac{d\Pi}{dt} = -\frac{1}{\tau_R}\Pi \tag{12.30}$$

with the well-known solution

$$\Pi = \Pi_0 \exp\left(-\frac{t}{\tau_R}\right) . \tag{12.31}$$

The above equations also give the kinetics of relaxation of the deformation (for $\Pi = 0$) in an initially stressed body when it is described by the Kelvin-Voigt equation.

From a more general point of view the relaxation of strains in a Maxwell body, the relaxation of deformations in a Kelvin-Voigt body or relaxation processes in real systems – relaxation of strains in glasses or the retarded response of glass-forming melts to external disturbances – can be treated either as an evolution of the frozen-in system towards equilibrium (relaxation as a process of glass stabilization) or as the response of a dissipative system to a time-limited external influence. Thus the rheology of glass-forming melts, which determines the kinetics of the most significant processes in under-cooled melts (their vitrification and crystallization), gives also an illustration of the behavior of dissipative systems, in general. This similarity becomes also evident from a comparison of Eqs. (12.15), (12.17) and (12.30) with the derivations given in Sect. 3.9.

From Eqs. (12.5) and (12.6) it is obvious that in Maxwell's kinetics of relaxation the assumption of a Newtonian flow behavior (with constant values of η and τ_R) of the systems under consideration is inherent. A straightforward generalization of the Maxwellian relaxation kinetics can be given, consequently, by introducing for real systems an apparent relaxation time, $\tau_R^{(app)}$, as

$$\tau_R^{(app)} = \frac{\eta_{(app)}}{G^*} \ . \tag{12.32}$$

By this procedure, determining, in analogy to Eq. (12.30), relaxation via the relation

$$\frac{d\Pi}{dt} = -\frac{\Pi}{\eta_{(app)}} \tag{12.33}$$

a large variety of possible solutions, accounting for the real flow behavior of viscoelastic bodies, may be achieved by using $\eta_{(app)}$-dependencies as discussed in the previous section. In this way, in the already mentioned paper by Gutzow et al. (1993) [333] a detailed analysis of different solutions is given for possible models of dilatant and pseudo-plastic behavior of real liquids.

As an example, the de Waele-Ostwald equation gives for $n = 2$ a dependence of the form

$$\frac{1}{\Pi(t)} - \frac{1}{\Pi(0)} = A_1 \frac{t}{\tau_0} \tag{12.34}$$

corresponding to the empirically established formula by Adams and Williamson [6, 925]. The differential equation, giving a relaxation kinetics as described by Eq. (12.34), is of the form

$$\frac{d\Pi}{dt} = -\frac{1}{\tau_0}\Pi^2 \ . \tag{12.35}$$

It follows that the Maxwellian type of relaxation kinetics, according to which the rate of stress relaxation is proportional to the stress itself, can be considered only as the simplest possible assumption. Moreover, while in the original Maxwellian relaxation kinetics (Eq. (12.30)) the relaxation time, τ_R, is considered as a constant, in the generalized dependencies this is not the case. According to Eq. (12.33), $\tau_R^{(app)}$ depends, in general, on the stress, Π. But since the stress is a function of time, $\tau_R^{(app)}$

also becomes time dependent. This argumentation allows us to rewrite $\tau_R^{(app)}$ in the form $\tau_R^{(app)} = \tau_R \tau^*(t)$ and with Eq. (12.33) the result

$$\frac{d\Pi}{dt} = -\frac{A_2}{\tau_R \tau^*(t)} \Pi \tag{12.36}$$

is obtained, where A_2 and τ_R are constants and $\tau^*(t)$ is a function of time, determined by the kind of rheological behavior of the considered liquid. In the case where

$$\tau^*(t) = t^p \tag{12.37}$$

holds (the effective relaxation time increases with time by a power law), p being a real number smaller than one, an equation for the relaxation behavior proposed first by Kohlrausch (1876) [462] is obtained as a special case. It reads

$$\Pi = \Pi(0) \exp\left[-\left(\frac{t}{\tau_k}\right)^b\right], \qquad b = 1 - p, \qquad \tau_k = \left(\frac{\tau_R b}{A_2}\right)^{1/b}. \tag{12.38}$$

The equation given above is usually denoted as the fractional (or stretched) exponent relaxation function. It is used with success for a description of relaxation of glass-forming melts.

According to the experimental evidence collected by Mazurin (1986) [543] values of b of the order $b = (0.5 - 0.75)$ (i.e., $p = (0.5 - 0.25)$) have to be expected for glass-forming liquids; for polymers, lower b-values are found in the range $b = (0.3 - 0.35)$ (i.e., $p = (0.7 - 0.65)$). As shown by Gutzow et al. (1993) [332] such values of the b-parameter are equivalent to respective n-values in the de Waele-Ostwald equation ($n \cong p + 1$). Recalling that for relaxation in glass-forming liquids $n = 1.5$ for the de Waele-Ostwald equation gives the best fit to experimental results, therefore the above mentioned b-values are easily explained.

12.6 Molecular Models of Viscous Flow

In the discussion of molecular models of viscous flow and molecular relaxation of glass-forming liquids it is usually assumed (see Sanditov and Bartenev (1982) [683]) that two independent steps are involved in this process, described by two different probabilities:

- The probability of activation of a molecule to break the bonds with the neighboring molecules and
- The probability that in the vicinity of an activated molecule, a sufficiently large void is formed, so that N_f building units responsible for the flow may enter it.

In accordance with earlier models by Eyring (see Glasstone et al. (1941) [255]) for the probability of activation of a molecule a constant activation energy, U_0, is supposed proportional to the enthalpy of evaporation, $\Delta H_{(ev)}$, of the liquid.

The second step in molecular models of viscous flow is connected with the determination of the probability of formation of a sufficiently large void in the liquid, equal or larger than the volume of N_f molecules, in the vicinity of the activated unit. Such calculations were performed in two variants by Cohen and Turnbull (1959) [137] and by Bueche (see Bueche (1962) [109]). It turns out that this probability depends exponentially on the reciprocal of the relative free volume $1/\xi(T)$ as assumed, for example, in Doolittle's empirical equation, Eq. (2.90). In this way, equations of such a type reflect mainly the process of hole formation as essential in the determination of the viscosity. The generalized molecular description of flow processes in glass-forming melts, taking into account both above mentioned steps in the description of flow, results in temperature dependencies of the viscosity which may be written in a form similar to the Macedo-Litovitz equation, Eq. (2.96), as

$$\eta(T) = \eta_0 \exp\left(\frac{U_0}{k_B T}\right) \exp\left(\frac{B}{\xi(T)}\right) , \qquad (12.39)$$

where B depends on the number of molecules forming an average flow unit. According to an analysis made by Gutzow et al. (1985) [330] B varies, in general, from 1 (noble gas melts, liquid metals) to 6 (liquids formed by associating organic compounds).

The Vogel-Fulcher-Tammann equation, Eq. (2.84), follows from the above equation, if ξ is of the form $\xi \propto (T - T_\infty)$. Such a dependence has been discussed, in fact, already in one of the previous sections (cf. Eq. (3.32)). Replacing ξ according to Eq. (5.78) by the configurational entropy of the liquid Eq. (12.34) may be rewritten in the form

$$\eta(T) = \eta_0 \exp\left(\frac{U_0}{k_B T}\right) \exp\left(2.5 \frac{\Delta S_m}{\Delta S(T)}\right) . \qquad (12.40)$$

For simple liquids $\Delta S_m \cong R$ holds. The second part of Eq. (12.40) is equivalent to a relation derived by Adam and Gibbs (1965) [5]. The above combination was proposed and discussed in detail by Gutzow et al. (1985) [330].

Summarizing, we may conclude that, as already mentioned in Chap. 2, temperature dependencies of the viscosity, involving only one activation energy and one exponential term reflect only one side of the mechanism of viscous flow (like Frenkel's original equation Eq. (2.78) derived in the framework of free volume and hole theories of liquids). Additional processes which have to be taken also into account lead to additional exponential terms as described above. Other mechanisms of viscous flow in glass-forming liquids lead to temperature dependencies of the form as given with Eqs. (2.92) and (2.95). Such models are essentially based on Anderson's idea (1958) [10] of treating structural disorder in terms of an ensemble of energetic barriers of different heights (while an ordered system is characterized by only one energetic barrier). By such an approach, developed in a series of papers by Avramov and Milchev [20, 22, 26, 559], the process of self-diffusion in both ordered and disordered structures may be treated in a straightforward way; in disordered

Fig. 12.5 Temperature
dependence of the time of
molecular relaxation in the
vicinity of the glass transition
temperature, T_g
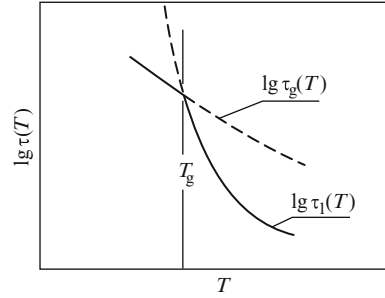
structures the activated complex may use different diffusion channels for an escape
while in an ordered state only one reaction possibility exists.

Also some additional conclusions can be drawn from the above-given deriva-
tions. Upon vitrification $\Delta S(T)$ (in Eq. (12.40)) or $\xi(T)$ (in Eq. (12.39)) are frozen
in. Consequently, below the temperature of vitrification, we have to expect

$$\left(\frac{d\eta(T)}{d(1/T)}\right)_{T<T_g} = \frac{U_0}{k_B} = \text{const.} \tag{12.41}$$

in agreement with experimental findings (cf. Figs. 2.14, 2.16 and 12.5) and with
more general considerations. It is essential to note that the freezing-in process also
implies constant values of the activation energy below T_g (see Gutzow, Dobreva, and
Pye (1994) [335]). The salient point of the $\log\eta$ vs $(1/T)$-curve gives an additional
kinetic method of determination of the temperature of vitrification (see Mazurin
(1986) [543]). The ratio

$$\Theta = \frac{\left(\dfrac{d\log\eta}{d\frac{1}{T}}\right)_{T\leq T_g}}{\left(\dfrac{d\log\eta}{d\frac{1}{T}}\right)_{T\to T_g}} \tag{12.42}$$

determines the so-called Narayanaswami coefficient. Methods of determination of
this coefficient are discussed by Avramov et al. (1987 [29], 1988 [31]). It has values
of the order of 0.5.

12.7   Molecular Models of Flow of Liquids Under Stress

The flow of a liquid under stress can be analyzed in terms of a molecular model
developed by Prandtl (1928) [644] in the framework of the absolute rate theory
(Glasstone et al. (1941) [255]). It gives an instructive explanation of Non-Newtonian
behavior of pseudoplastic materials. Both Prandtl and Eyring assumed that in a
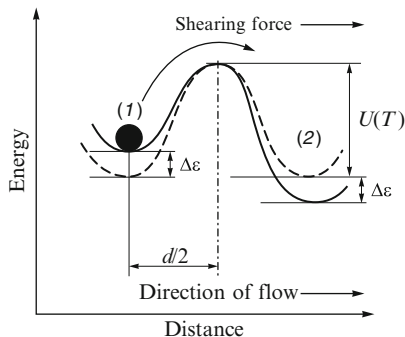
Fig. 12.6 The Prandtl-Eyring model for the change of the activation energy in a pseudo-plastic liquid under applied stress. For zero stresses *(dashed curve)* the probability of motion of a particle of the liquid is the same for both considered possible directions, while under stresses *(full curve)* a preferred direction of flow exists

liquid subjected to tangential stresses the activation energy, $U(T)$, for self-diffusion decreases in the direction of the applied stresses, Π, by a quantity $\Delta\varepsilon$ proportional to the stress. In the opposite direction $U(T)$ increases by the same value (see Fig. 12.6). Thus, the rate of net flow in the direction of the applied stress becomes equal to

$$\frac{d\gamma}{dt} = \frac{2D}{d^2} \sinh\left(\frac{d^3}{2k_B T}\Pi\right) , \tag{12.43}$$

where D is the self-diffusion coefficient of the ambient phase building units realizing the flow and having a volume of the order d^3 (the so-called "viscous" volume). The "viscous" volume can be expected to be proportional to the volume d_0^3 of the building units of the liquid. In the paper by Gutzow et al. (1993) [332], a generalization of the above model is given accounting in addition to energetic considerations also for entropy effects in viscous flow. This approach also allows us a description of the flow of dilatant liquids in terms of the same activated complex model.

Additional, more or less complicated, molecular models describing flow processes in polymer liquid solutions under various conditions can be traced mainly in literature on polymers. Here of particular importance are models describing the flow of polymer molecule coils through "tubes" formed by surrounding solute molecules (tube and coil models, see Doi (1980) [178]). The Prandtl-Eyring model, although leading to considerable difficulties in application to polymer liquid flow (where entropy effects are dominating), gives a safe basis in correlating experimental evidence on Non-Newtonian flow of inorganic and metallic glass-forming melts (see the evidence collected in a paper by Gutzow et al. (1993) [332]; the results of Li and Uhlmann (1970) [508] on silicate glasses, of Wäsche and Brückner (1986) [912] for phosphate melts and of Russev et al. (1990) [677] on metallic glass-forming alloys).

12.8   Kinetics of Nucleation and Growth in Viscoelastic Media

The incorporation of specific rheological viscoelastic properties of the matrix into the description of the segregation kinetics in glass-forming melts was carried out in a series of papers by Pascova et al. and Schmelzer et al. (see [627, 628, 710, 713, 714]). It was shown, in particular that the rate of growth of clusters in segregation processes of silver chloride particles in a highly viscous melt can be described by an equation of the form

$$\frac{dV}{dt} = \left(\frac{dV}{dt}\right)_N \exp\left(-\frac{t}{\tau_{(eff)}}\right) , \tag{12.44}$$

where $(dV/dt)_N$ is the rate of growth of a cluster in a perfect Newtonian liquid and $\tau_{(eff)}$ a parameter depending on the properties of the liquid. The integration of this equation results in a Kelvin-Voigt type behavior of the growth kinetics and also in a qualitative change of the coarsening behavior as shown in Fig. 9.3. Moreover, peculiarities in the time evolution of the cluster size distribution of segregating particles can be interpreted based on the same theoretical considerations (cf. Bartels et al. (1991) [43]).

   This approach gives a new, more general way of interpreting crystallization and segregation phenomena in glass-forming liquids, in particular, in the vicinity of T_g. The mentioned effects become essential in the determination of the growth kinetics for segregation processes when the self-diffusion coefficient of the segregating particles is considerably higher than the respective coefficient for the matrix building units [713, 714]. For nucleation processes themselves the effect is of less importance since the velocity of deterministic growth of clusters of near-critical sizes is practically equal to zero. These problems are discussed in detail in the cited papers.